

Copper-doping effects in electronic structure and spectral properties of SmNi_5

Yu.V. Knyazev¹, A.V. Lukoyanov^{1,2}, Yu.I. Kuz'min¹, and A.G. Kuchin¹

¹*Institute of Metal Physic UD of RAS, S. Kovalevskoy, 18, Ekaterinburg 620990, Russia*

E-mail: knyazev@imp.uran.ru

²*Ural Federal University, Mira, 19, Ekaterinburg 620002, Russia*

Received May 14, 2015, published online October 23, 2015

The electronic structure and optical properties of the $\text{SmNi}_{5-x}\text{Cu}_x$ ($x = 0, 1, 2$) compounds are studied. The band spectra of the studied intermetallics were calculated with LDA+ U +SO method supplementing the local density approximation with a correction for strong electron interaction on the shell of the rare-earth element. Optical properties were studied by ellipsometry method in the wide wavelength range. It was found that the substitution of copper for nickel leads to local changes in the optical conductivity spectra. Both the spectroscopic measurements and theoretical calculations demonstrate the presence of a broad absorption band around 4 eV associated with the $\text{Cu } 3d \rightarrow \text{Ni } 3d$ electron transitions and increasing with the grown of copper content. The experimental dispersion curves of optical conductivity in the interband absorption region were interpreted using the results of the calculations.

PACS: **71.20.-b** Electron density of states and band structure of crystalline solids;

71.20.Eh Rare-earth metals and alloys;

78.30.-j Infrared and Raman spectra;

78.40.-q Absorption and reflection spectra: visible and ultraviolet.

Keywords: rare-earth compounds; intermetallics, optical properties; electronic structure.

Introduction

The RNi_5 group of intermetallic compounds (where R is a rare earth) and their substitutional derivatives have been extensively studied because of a variety of interesting properties promising for practical applications, such as magnetocaloric effect, hydrogen storage capacity, magnetic anisotropy and high coercivity [1–6]. Their diverse magnetic and electronic characteristics are associated with both localized moments of R atoms and itinerant electrons of Ni atoms in hexagonal CaCu_5 -type structure. Besides studying the properties of binary compounds, studying the influence of partial substitution of the rare earth or the nickel on the physical properties and the electronic structure also attracted considerable attention. For example, substitution of Ni by some of p - or d -elements in RNi_5 can significantly affect some properties owing to changes in the electronic structure, crystal field effects and exchange interaction. In particular, various pseudobinary $\text{RNi}_{5-x}\text{M}_x$ compounds with $\text{M} = \text{Al, Ga, Si and Cu}$, as shown in numerous investigations, exhibit substantial concentration dependences of the crystalline, electronic, magnetic and

thermodynamic properties comparing to the parent compounds. Study of these materials is of special interest due to their ability to absorb and store atomic hydrogen. It was found that substitution of nickel in binary intermetallics by certain metals can drastically influence the hydrogen sorption characteristics of the prototype compound.

Significant modifications of some properties owing to the doping effect were found also in ferromagnetic $\text{SmNi}_{5-x}\text{Cu}_x$ system (the Curie temperature T_C for binary SmNi_5 is 30 K [2]). The substitution of Cu for Ni is accompanied by decreasing of spontaneous magnetic moment and increasing of coercive force, which indicates the presence of crystal electric field effect [2]. Also it was shown that T_C displays nonmonotonic concentration dependence with the maximum at $x \sim 1$. In ternary SmNi_4Cu compound the x-ray photoemission spectroscopy of the valence band region revealed peculiarities related to the Cu impurity [7]. To explain the experimental data, one needs more detailed investigations on the electronic structure of the $\text{SmNi}_{5-x}\text{Cu}_x$ series for different x .

In this paper we report the results of band structure calculations of intermetallics of the $\text{SmNi}_{5-x}\text{Cu}_x$ ($x = 0, 1, 2$)

system with the aim to obtain a deeper insight into their electronic structures. In addition to electronic structure analysis, the optical measurements were performed. Optical spectroscopy is a suitable technique to study the energy and the intensity of the electronic excitations as well as the changes in the density and the mobility of the carriers because it allows the determination of the plasma and relaxation frequencies. The experimental spectral data were analyzed in accordance with the computed band structures.

Experimental and calculation details

The polycrystalline samples of $\text{SmNi}_{5-x}\text{Cu}_x$ were synthesized by a standard induction melting procedure in the argon protective atmosphere using induction furnace, with stoichiometric quantities of the reactant elements of at least 99.9% purity. The resulting ingots were inverted and melted several times to insure a better homogeneity. To obtain a single-phase state, the annealing at $\sim 1100^\circ\text{C}$ was performed for 10 h. The prepared samples were checked for phase purity using standard powder x-ray diffraction method. The hexagonal CaCu_5 -type crystal structure of space group $P6/mmm$ was confirmed from diffraction spectrum. Rare-earth atoms occupy the $1a$ site (0,0,0), two Ni_2 atoms are in the $2c$ sites ($1/3, 2/3, 0$) and three Ni_2 atoms are in $3g$ sites ($1/2, 0, 1/2$). The obtained lattice parameters were used in our theoretical calculations.

The studies of the optical properties were performed at room temperature in the wavelength range of $\lambda = 0.22\text{--}16\ \mu\text{m}$ (photon energies $E = 5.64\text{--}0.078\ \text{eV}$). The optical constants, i.e., refractive index $n(\lambda)$ and absorption coefficient $k(\lambda)$ were derived from the ellipsometry measurements using the Beattie technique. Spectroscopic ellipsometry is based on the fact that the state of polarization of incident light is changed on reflection. This change is directly related to the dielectric function of reflecting material. Mirror samples surfaces were obtained by means of mechanical polishing with diamond pastes. The measured values n and k enable to determine a number of spectral functions that characterize the optical response of the medium, including the permittivity $\varepsilon = \varepsilon_1 - i\varepsilon_2$, reflectivity R and the most sensitive parameter, namely the optical conductivity $\sigma(\omega) = \varepsilon_2\omega/4\pi$ (ω is the frequency of light wave).

The electronic structure of $\text{SmNi}_{5-x}\text{Cu}_x$ compounds for $x = 0, 1, 2$ was calculated with the LDA+ U +SO method [8] in the framework of TB-LMTO-ASA (tight binding, linear muffin-tin orbital, atomic sphere approximation). The LDA+ U +SO supplements the local density approximation with the Hubbard U correction for strong electronic correlations and spin-orbit coupling in the $4f$ shell of samarium. The values of direct Coulomb $U = 6.3\ \text{eV}$ and exchange Hund $J = 0.6\ \text{eV}$ parameters were calculated in additional constrained LDA calculations [9]. In all calculations we used a \mathbf{k} -mesh of $512 = 8 \times 8 \times 8$ points and muffin-tin radii

$r(\text{Sm}) = 3.6\ \text{a.u.}$, $r(\text{Ni,Cu}) = 2.7\ \text{a.u.}$ In order to account for Cu in different positions, self-consistent total and partial densities of electronic states (DOS) were averaged over all possible configurations of Cu atoms substitutions for Ni in the unit cell.

In the calculations we obtained significant magnetic moments of samarium and almost negligible moments of nickel with the maximum orbital moment of $0.05\ \mu_B$ on the Ni ions similar to previous experimental and theoretical data, e.g., [10]. Since spin-orbit coupling in the $4f$ shell of samarium was explicitly taken into account in the LDA+ U +SO method, total magnetic moment can be calculated including the orbital component [11]. The following configuration of the Sm ions was found for all Cu concentrations: $2S = 4.8$, $L = 4.7$, $J = 2.3$, $g = 0.27$, $gJ = 0.63$. These values are rather close to Sm^{3+} : $2S = 5.1$, $L = 5.0$, $J = 2.45$, $g = 0.286$, $gJ = 0.7$.

Total and partial (for Sm $4f$ and Cu $3d$ electrons) densities of states for $\text{SmNi}_{5-x}\text{Cu}_x$ ($x = 0, 1, 2$) compounds are shown in Fig. 1. The DOS up to energy of 4 eV below the Fermi level E_F are primarily associated with the Ni $3d$ electrons. The sharp dark peaks belong to the partial densities of Sm empty and filled $4f$ states above and below the E_F , respectively. The grey regions in Figs. 1(b),(c) correspond to the filled Cu $3d$ states whose DOS are largest in the range $-2\text{--}4\ \text{eV}$. The intensity and extension of this structure become more significant when substituting Ni

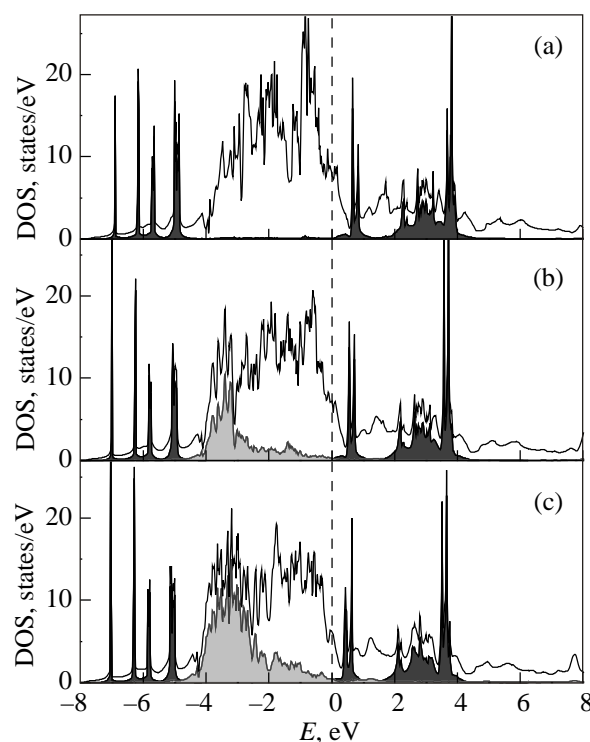


Fig. 1. Total (solid curve) and partial for Cu $3d$ (grey regions) and Sm $4f$ (dark regions) densities of states calculated for SmNi_5 (a), SmNi_4Cu (b) and SmNi_3Cu_2 (c) compounds in the framework of LDA+ U +SO method. The Fermi level corresponds to zero on the energy scale.

by Cu atoms increases. The calculated energy maximum of the localization of the impurity Cu 3*d* electron band centered near 3.5 eV is close to the previously obtained values for other compounds of this type, where the Ni atoms are substituted by Cu [12–14]. The evolution of the electronic structure when replacing Ni by Cu is illustrated in Figs. 1(b),(c). An increase in the concentration of Cu atoms leads to a modification of the spectral profile of the total DOS mostly below E_F . These changes manifest themselves in the fact that the broad minimum in the range of $-1 \dots -2$ eV between two groups of peaks observed in SmNi₅ is less pronounced in the ternary compounds. Besides that, the doping of the Cu atoms leads to essential enhancement of the total DOS in the energy region below ~ -3 eV.

It should be noted that the calculated density of states for ternary SmNi₄Cu is in good agreement with the experimental x-ray photoemission spectrum of this compound [7]. The localization and width of the main structural features revealed in this spectrum due to the Ni, Cu 3*d* states and Sm 4*f* states below the Fermi level are close to those obtained in our calculation. The decrease of DOS values at E_F going from $x = 0$ to $x = 2$ follows the same trend as the low-temperature magnetic susceptibility and heat capacity of these type compounds.

Result and discussion

Figure 2 shows the experimental dependences $n(\lambda)$ and $k(\lambda)$ for the SmNi_{5-x}Cu_x ($x = 0, 1, 2$) compounds. Over most of the wavelength range, except for the interval $\lambda < 1.5$ μm , the values of these parameters increase monotonically. Besides that, in the whole spectral region $k > n$, such a relation is inherent for a media with metallic conductivity. Typical

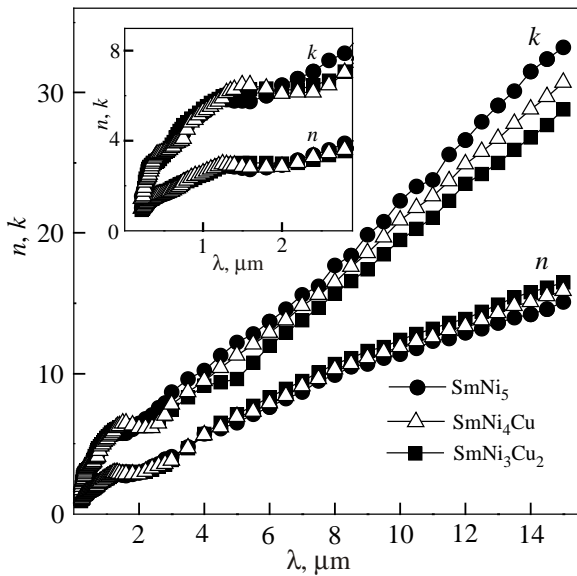


Fig. 2. Dependences of the refractive index n and absorption coefficient k on the wavelength of the incident light for SmNi₅, SmNi₄Cu and SmNi₃Cu₂ compounds. The inset shows the short-wavelength range.

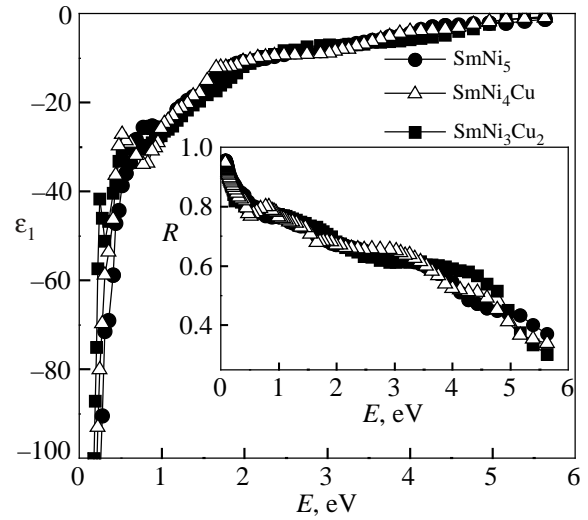


Fig. 3. Energy dependences of the real part of the permittivity and reflectivity (inset) of the SmNi₅, SmNi₄Cu and SmNi₃Cu₂ compounds.

metal-like behavior was observed also in the $\epsilon_1(E)$ and $R(E)$ dependences (see Fig. 3): the ϵ_1 values are negative in the entire energy range, while R tends to unity in the low-photon energy interval. The low-frequency growth of $R(E)$, as well as large and negative values of ϵ_1 , are stipulated by the intraband (Drude-type) light absorption. The intraband absorption is determined by the kinetic parameters of the conduction electrons — the relaxation γ and plasma ω_p frequencies. The relaxation frequency $\gamma = \epsilon_2 \omega / \epsilon_1$ additively takes into account all types of electron scattering upon excitation by the electromagnetic field, and in the limit $\omega \rightarrow 0$ it is determined by the static electrical resistivity. The squared plasma frequency $\omega_p^2 = \omega^2 (\epsilon_1^2 + \epsilon_2^2) / \epsilon_1$ is proportional to the Fermi velocity of electrons and their concentration. It is known [15] that in the single-electron approximation for an arbitrary dispersion relation $E(k)$ the ω_p^2 is proportional to the density of states at E_F . In the long-wavelength region $\lambda > 10$ μm , the γ and ω_p^2 parameters are frequency independent being stabilized at the values: $\gamma = 1.4 \cdot 10^{14} \text{ s}^{-1}$, $\omega_p^2 = 34.4 \cdot 10^{30} \text{ s}^{-2}$ (SmNi₅), $\gamma = 1.8 \cdot 10^{14} \text{ s}^{-1}$, $\omega_p^2 = 32.6 \cdot 10^{30} \text{ s}^{-2}$ (SmNi₄Cu) and $\gamma = 2.3 \cdot 10^{14} \text{ s}^{-1}$, $\omega_p^2 = 31.3 \cdot 10^{30} \text{ s}^{-2}$ (SmNi₃Cu₂). As one can see, the dependence $\gamma(x)$ for the studied system tends to increase, pointing out a direct effect of the Cu-doping on this parameter. The dependence $\omega_p^2(x)$ indicated that DOS for the studied compounds shows the tendency of reduction which is in a qualitative agreement with the band calculations. The values ω_p^2 were used to estimate the concentration of conduction electrons as $N = \omega_p^2 m / 4\pi e^2$ (m and e are the mass and the charge of free electron, respectively), which gave us: $N = 1.05 \cdot 10^{22} \text{ cm}^{-3}$ (SmNi₅), $N = 0.99 \cdot 10^{22} \text{ cm}^{-3}$ (SmNi₄Cu), $N = 0.95 \cdot 10^{22} \text{ cm}^{-3}$ (SmNi₃Cu₂).

In Fig. 4 the experimental optical conductivity spectra $\sigma(E)$ of these compounds are given (note that the curves

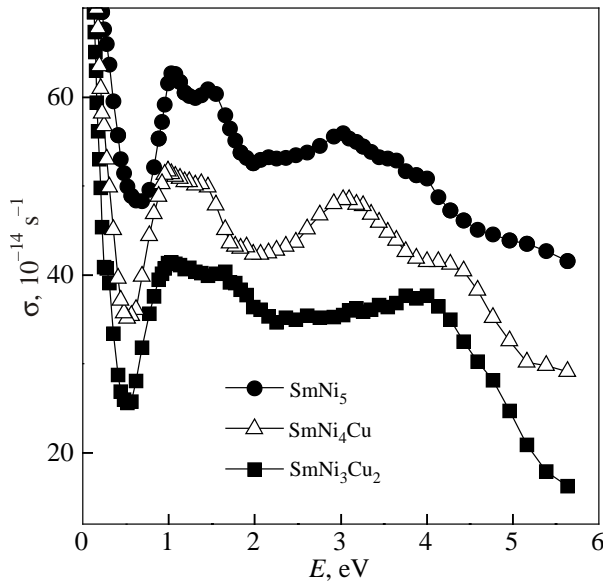


Fig. 4. Energy dependences of the optical conductivity of $\text{SmNi}_{5-x}\text{Cu}_x$ ($x = 0, 1, 2$) compounds. The curves are shifted upward along the ordinate axis relative to one another by 10 units.

are shifted with respect to each other along the vertical axis by 10 units). In the low-energy range a monotonic growth of $\sigma(E)$ is related to the Drude-type of electron excitation, $\sigma_D = \omega_p^2 \gamma / 4\pi(\omega^2 + \gamma^2)$. Above ~ 0.5 eV the shape of $\sigma(E)$ dependence indicates the dominant role of interband absorption. The spectra of the optical conductivity for all alloys in this region are characterized by the broad asymmetrical absorption band with the abrupt low-energy edge and some maximum, which intensity and position depend on the compound composition. It can be seen that the absorption band has almost the same width for the all studied compounds, whereas its structure is substantially transformed with variation in the amount of the impurities. In particular, the peak located at the energy ~ 3 eV in the spectrums $\sigma(E)$ of SmNi_5 and SmNi_4Cu compounds disappeared in the corresponding dependence for SmNi_3Cu_2 . The maxima near 4 eV, in turn, are conspicuous only in the $\sigma(E)$ curves of the ternary alloys. The formation of high-energy maxima is connected with the substantial changes in the electronic energy structure of compounds upon substitution Cu for Ni atoms. The localization of these features in the experimental $\sigma(E)$ spectra and the enhancement of their intensities with the increase of Cu content are correspondent to the theoretical DOS in Fig. 1. The similar maxima centered at ~ 4 eV were also found in optical conductivities of some $\text{RNi}_{5-x}\text{Cu}_x$ alloys [12–14] and identified as $\text{Cu } 3d \rightarrow \text{Ni } 3d$ transitions. According to the calculated DOS, the formation of intense absorption structures in the range $E < 3.5$ eV can be related mainly with the $\text{Ni } 3d \rightarrow \text{Ni } 3d$, $\text{Sm } 4f$ electron transitions.

The obtained DOS of $\text{SmNi}_{5-x}\text{Cu}_x$ ($x = 0, 1, 2$) compounds were used to interpret the experimental data. The interband optical conductivities were calculated directly from

the electronic structure through the convolution of the total DOS both below and above the E_F . The calculations were performed in approximation that the direct and indirect transitions are equally probable. The results of such calculations are given in Fig. 5 (shown in arbitrary units) together with the experimental interband contributions to the optical conductivity $\sigma_{\text{ib}} = \sigma(E) - \sigma_D(E)$. The calculations for all compounds predict the existence of a strong absorption region up to 6 eV, which is formed by electronic transitions between the states characterized by larger values of the total DOS. Note that calculations showed the presence of the broad maxima near 4 eV for SmNi_4Cu and SmNi_3Cu_2 compounds. There are also shown the partial contributions to the interband optical conductivity from quantum transitions involving electrons of the Sm 4f (dashed lines) and Cu 3d bands (dash-dotted lines). Dotted lines in Fig. 5 identify the Drude contribution. For all the alloys the fine structure in $\sigma_{\text{ib}}(E)$ spectra obtained from the total DOS is qualitatively similar to the corresponding dispersion curves determined by the partial contributions involving Sm 4f electrons ($\text{Ni } 3d \rightarrow \text{Sm } 4f$ and $\text{Cu } 3d \rightarrow \text{Sm } 4f$ transitions). This suggests a significant role played by Sm 4f electrons in the interband absorption in $\text{SmNi}_{5-x}\text{Cu}_x$ compounds.

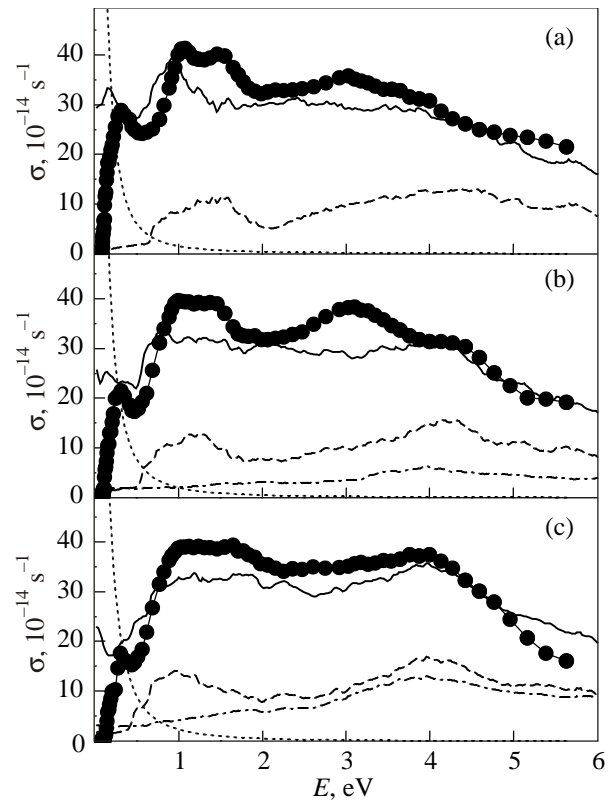


Fig. 5. Interband optical conductivity spectra of SmNi_5 (a), SmNi_4Cu (b) and SmNi_3Cu_2 (c). Circles refer to experiment and the solid curve corresponds to calculations in arbitrary units. Dashed and dash-dotted curves represent the partial contributions from the transitions involving the Sm 4f electron bands and Cu 3d bands, respectively. Dotted lines show the Drude contribution.

A comparison of the experimental dependences of interband optical conductivity with the theoretical ones shows both their certain similarity (the position of some features and the same energy range of quantum absorption) and distinctions, which manifest themselves mainly in the curves for the SmNi₄Cu. On the whole, we can conclude that the energy dispersion of $\sigma(E)$ of SmNi_{5-x}Cu_x compounds with $x = 0, 1, 2$ within the fundamental absorption band is adequately described by the calculated band structure.

Conclusions

The evolution of the electronic structure and optical properties of SmNi_{5-x}Cu_x ($x = 0, 1, 2$) compounds by the substitution of copper for nickel atoms has been investigated. The energy dependences of the total and partial electronic densities of states have been calculated by LDA+*U*+SO method taking into account strong electron-electron interactions in the Sm 4*f* shell. The nature of electronic states involved in formation of interband optical absorption spectra in the energy range $E_F \pm 6$ eV has been determined. Optical properties were studied ellipsometrically in a broad spectral range. It has been shown that the frequency dependences of the optical conductivities in the quantum light absorption region are satisfactory explained in terms of the calculated densities of electronic states. The spectral data in the infrared region were used to obtain the relaxation and plasma frequencies of conduction electrons.

The research was carried out within the state assignment of FASO of Russia (theme "Electron" No. 01201463326), supported in part by RFBR (projects 13-02-00256 and 13-02-00050), Program of UrB RAS (project 15-8-2-4) and the Dynasty Foundation. Some results reported in this work were obtained using "Uran" supercomputer of IMM UrB RAS.

1. D.L. Rocco, J.S. Amaral, J.V. Leitão, V.S. Amaral, M.S. Reis, R.P. Fernandes, A.M. Pereira, J.P. Araújo, N.V. Martins, P.B. Tavares, and A.A. Coelho, *Phys. Rev. B* **79**, 014428 (2009).
2. A.G. Kuchin, A.S. Ermolenko, Yu.A. Kulikov, V.I. Khrabrov, E.V. Rosenfeld, G.M. Makarova, T.P. Lapina, and Ye.V. Belozarov, *J. Magn. Magn. Mater.* **303**, 119 (2006).
3. J. Yao, O. Isnard, A.V. Morozkin, T.I. Ivanova, Yu.S. Koshkid'ko, A.E. Bogdanov, S.A. Nikitin, and W. Suski, *J. Solid State Chem.* **222**, 123 (2015).
4. D.A. Joshi, C.V. Tomy, D.S. Rana, R. Nagarajan and S.K. Malik, *Solid State Commun.* **137**, 225 (2006).
5. H. Senoh, N. Takeichi, T. Kiyobayashi, H. Tanaka, H.T. Takeshita, T. Oishi, and N. Kuriyama, *J. Alloys Compd.* **404-406**, 47 (2005).
6. X. Wang, R. Chen, Y. Zhang, C. Chen, and Q. Wang, *Mater. Lett.* **61**, 1101 (2007).
7. T. Toliński, G. Chełkowska, and A. Kowalczyk, *Physica B: Condens. Matter* **378-380**, 1114 (2006).
8. A.O. Shorikov, A.V. Lukoyanov, M.A. Korotin, and V.I. Anisimov, *Phys. Rev. B* **72**, 024458 (2005).
9. V.I. Anisimov and O. Gunnarsson, *Phys. Rev. B* **43**, 7570 (1991).
10. A. Langenberg, K. Hirsch, A. Ławicki, V. Zamudio-Bayer, M. Niemeyer, P. Chmiela, B. Langbehn, A. Terasaki, B.V. Issendorff, and J.T. Lau, *Phys. Rev. B* **90**, 184420 (2014).
11. Yu.V. Knyazev, Yu.I. Kuz'min, A.G. Kuchin, A.V. Lukoyanov, and I.A. Nekrasov, *J. Phys.: Condens. Matter* **19**, 116215 (2007).
12. Yu.V. Knyazev, A.V. Lukoyanov, Yu.I. Kuz'min, and A.G. Kuchin, *J. Alloys Compd.* **509**, 5238 (2011).
13. I.A. Nekrasov, E.E. Kokorina, V.A. Galkin, Yu.I. Kuz'min, Yu.V. Knyazev, and A.G. Kuchin, *Physica B: Condens. Matter* **407**, 3600 (2012).
14. Yu.V. Knyazev, A.V. Lukoyanov, Yu.I. Kuz'min, and A.G. Kuchin, *Phys. Solid State* **55**, 2191 (2013).
15. M.I. Kaganov and V.V. Slezov, *Zh. Exp. Teor. Fiz.* **32**, 1496 (1957).